Low-Temperature Chemical Vapor Deposition of Silver on Ag(111) Using $((CH_3)_3CCOCHCOC_3F_7)AgPEt_3$

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Abstract: The adsorption of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (fodH) and (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)(triethylphosphine)silver(I) ((fod)$AgPEt_3$) on Ag(111) has been studied using reflection absorption infrared spectroscopy and temperature programmed desorption techniques. fodH adsorbs molecularly in two adsorbed states. The first state adsorbs with its molecular plane parallel to the surface and desorbs at 250 K. The second adsorbed state is the condensed phase which desorbs at 197 K. The most interesting result of this work is that, at the lowest coverages, the first (fod)$AgPEt_3$ molecules adsorb parallel to the Ag(111) surface and dissociate at very low temperature. For higher doses, (fod)$AgPEt_3$ molecules are randomly oriented at low temperature. Upon heating of the sample, these molecules reorient their molecular plane to a position nearly perpendicular to the Ag(111) surface before their desorption at 290 K. The desorbing byproducts resulting from the dissociation of the flat-laying molecules are fodH at 200 K, CH_4 at 140 K, and PEt_3 at 135 and 170 K. At high temperature the desorption of HF was observed at 490 K and CO_2 around 600 K. The desorption of C_3F_7 and C_4H_9 radicals was also detected at this temperature.

Introduction

Metal–organic chemical vapor deposition (MOCVD) techniques have attracted much attention in the last few years. The main applications of CVD are conformal metal deposition[1] on shaped surfaces and selective deposition[2,3] at low temperature on patterned substrates used in microelectronic technology. The shrinking size of integrated circuits and the need for ultrafast interconnection metals have led to the need for replacement of tungsten and aluminum, metals which have resistivities of 5.6 and 2.8 $\mu\Omega$·cm, respectively, by metals having lower resistivities like copper (1.67 $\mu\Omega$·cm) and perhaps silver (1.59 $\mu\Omega$·cm).[4]

Several molecules have been used in copper CVD,[5,6] and the most promising are copper(I) β-diketonate complexes, since they can yield pure copper films under a variety of conditions.[7–9] The most widely used β-diketonate ligand in copper CVD is hexafluoroacetylacetonate (hfac) because this ligand forms stable and volatile complexes. The analogous silver complexes are, however, less stable or need a higher deposition temperature.[10–12] In this article we report the use of a new silver precursor which possesses the best combination of thermal stability and volatility yet known and so promises to be an excellent precursor for CVD of silver.

In particular, we report a study of the adsorption of (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)(triethylphosphine)silver(I) ((fod)$AgPEt_3$) on Ag(111). The Ag(111) crystal was used to study the reactivity of (fod)$AgPEt_3$ on a growing Ag film during CVD of silver. It was expected that a study of the surface chemistry of these complexes would give information on the mechanism of carbon contaminant incorporation into the deposited silver film as a result of ligand decomposition. Therefore, we report the results of the interaction of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione or fodH with Ag(111).

Experimental Section

The ultrahigh vacuum (UHV) system (base pressure $< 2 \times 10^{-10}$ Torr) used in this experiment was equipped with a turbomolecular pump (330 l/s), a sputtering gun for crystal cleaning, and a Hiden-601 mass spectrometer for temperature programmed desorption (TPD) measurements. The sample temperature was increased linearly with time at a rate, β, of 2 K·s^{-1}, while 16 masses were monitored during each TPD run. Reflection absorption infrared red spectroscopy (RAIRS) measurements were performed with a Mattson Cygnus-100 spectrometer. The resolution was set to 8 cm^{-1}, and the signal was averaged for 500 scans. The collection time of a spectrum was approximately 3 min. A narrow band mercury–cadmium–tellurium (MCT) detector was employed for data collection. Spectra-calc software was used for FTIR spectral deconvolution.

The sample was mounted on a cold finger which is similar to that described by Thiel,[13] with the only difference being that ours ends with three feedthroughs to hold two samples. The substrate used in this work was a Ag(111) crystal. This crystal was 1.5 cm in diameter and 3 mm thick. It was cut, polished, and oriented using standard methods. The Ag(111) sample was mounted between two tantalum wires set into two grooves located on the upper and lower edges of the crystal. A chromel-alumel thermocouple was inserted into a hole located on the side of the sample at an equal distance from the grooves.

The Ag(111) crystal was cleaned by repetitive cycles of argon sputtering and annealing in oxygen. The sputtering energy was 700

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eV with an ion current of 12−15 μA. The angle of sputtering was varied between 60° and 70° with respect to the surface normal. The sputtering of the sample was followed by annealing in oxygen at a pressure of 5×10^{-4} Torr and a temperature of 673 K. The final step was then a flash of the Ag(111) crystal to 900 K in vacuum after each sputtering−annealing cycle.[14−15] This surface showed a good LEED pattern.

1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-4,6-octanedione, abbreviated to fodH, was obtained from Aldrich Chemical Co. It was cleaned by repetitive freeze−pump−thaw cycles. The precursor (fod)AgPEt$_3$ was synthesised in our laboratories. Details of the synthesis method and the physical parameters of this precursor are given elsewhere.[16] This precursor is a yellow liquid at room temperature. The pressure during the adsorption of the precursor was kept below 1×10^{-9} Torr, and the temperature of the reservoir containing the precursor was maintained around 340 K. In order to make sure that the precursor was not over heated, two thermocouples were used to monitor the temperature of the tube and the reservoir. This doser is described elsewhere.[17] Prior to each admission of the precursor, the reservoir was pumped for several minutes and the shutter located at the end of the doser was closed to prevent surface contamination by any volatile species coming from the reservoir. The distance between the substrate and the doser end was approximately 1.5 cm.

Results and Discussion

Since the purity of the growing metallic films by CVD processes is directly related to the mechanisms governing the surface chemistry of the ligands, we have studied the adsorption of fodH on Ag(111).

Surface Reaction of fodH and (fod)AgPEt$_3$ on Ag(111). (A) Adsorption of fodH on Ag(111). TPD Results of fodH Adsorption on Ag(111). TPD results of the adsorption of fodH on Ag(111) at 90 K show one molecular desorption peak centered at 250 K for low exposure (Figure 1). This feature increases with exposure until it saturates and a second desorption peak appears at 197 K. The latter feature is related to the desorption from the multilayer whereas the former is attributed to the chemisorbed phase. The multilayer peak exhibits zeroth-order desorption kinetics, and the chemisorbed layer exhibits first-order desorption kinetics. On the basis of the Redhead equations,[18] the activation energy of desorption of the chemisorbed phase is 72 kJ·mol^{-1} assuming that the pre-exponential factor is 10^{13} s^{-1} for $\beta = 2$ K·s^{-1}. A number of fragments[19] were monitored during TPD cycles in order to establish if the adsorption of fodH on Ag(111) at low temperature is associative or dissociative. Figure 2 displays TPD spectra of mass 57 (C(CH$_3$)$_3$), 69 (CF$_3$), and 296 amu, which is the parent peak. All the detected ions arose from fodH fragmentation in the mass spectrometer. These results indicate then that fodH is adsorbed molecularly on Ag(111).

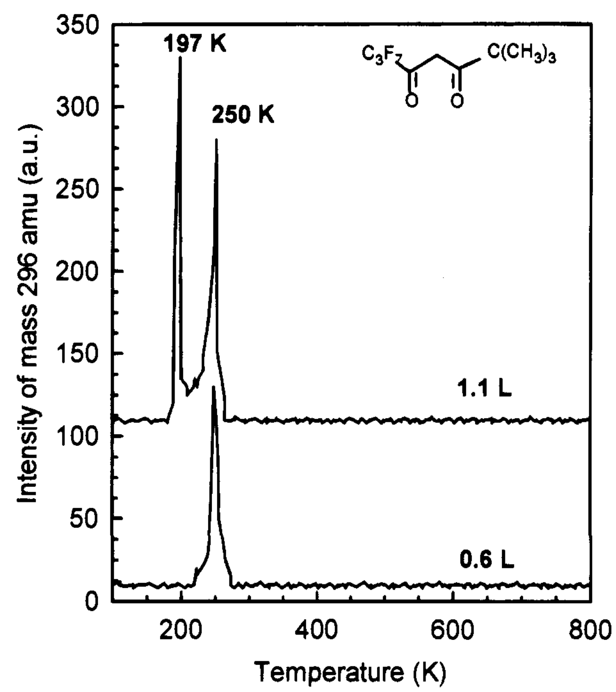

Figure 1. Temperature-programmed desorption spectra of adsorbed fodH (mass 296) on Ag(111) at 90 K as a function of the exposure of 0.6 and 1.1 L.

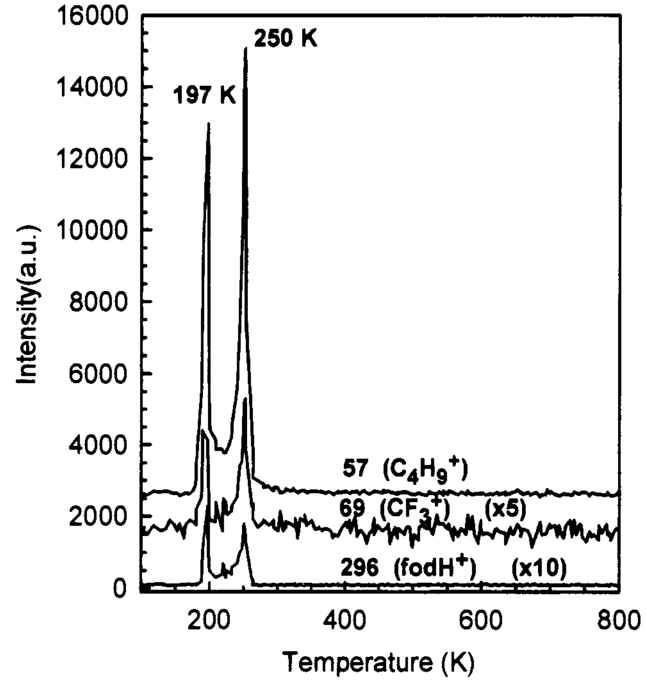

Figure 2. TPD spectra obtained after exposing a clean Ag(111) surface to 1.1 L of fodH at 90 K. Traces for masses 296 (fodH), 69 (CF$_3$), and 57 (C(CH$_3$)$_3$) are shown. The magnification factors are 10, 5, and 1, respectively.

RAIRS Results of fodH Adsorption on Ag(111). Figure 3 displays the vibrational spectra of the fodH/Ag(111) system at various exposures. The major change between lower and higher coverage is the appearance of the feature around 1600 cm^{-1} which corresponds to the ν(C=O) and ν(C=C) stretching modes. It is clear that at lower coverage these vibrational modes are completely absent or dipole inactive. According to the selection rules of the RAIRS technique,[20] only the active dipole moments with components perpendicular to the metallic surface are observed. The broad feature (near 1600 cm^{-1}) characterizing the higher exposure is due to the fact that dipoles are randomly oriented in the multilayer. These results suggest that the

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(19) The monitored masses during TPD runs for the fodH/Ag(111) system are 296, 268, 239, 211, 210, 169, 139, 127 120, 119, 100, 99, 98, 74, 70, 69, 59, 57, 50, 45, 42, 41, 31, 29, and 28 amu. In the case of (fod)AgPEt3 on Ag(111), monitored masses are 520, 296, 295, 402, 212, 211, 198, 192, 188, 170, 169, 154, 120, 119, 118, 109, 107, 100, 99, 98, 74, 70, 69, 59, 58, 57, 50, 47, 45, 44, 42, 41, 31, 30, 29, 28, 27, 20, and 16 amu.

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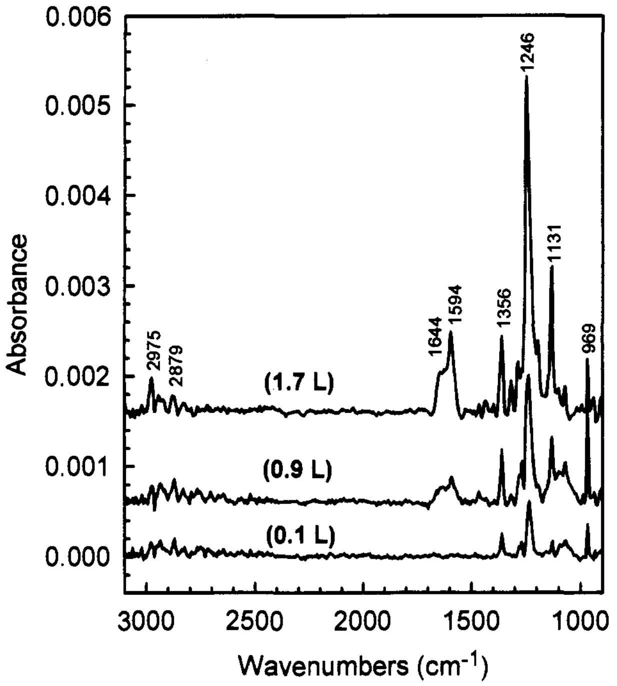

Figure 3. RAIR spectra after exposing Ag(111) at 90 K to 0.1, 0.9, and 1.7 L of fodH.

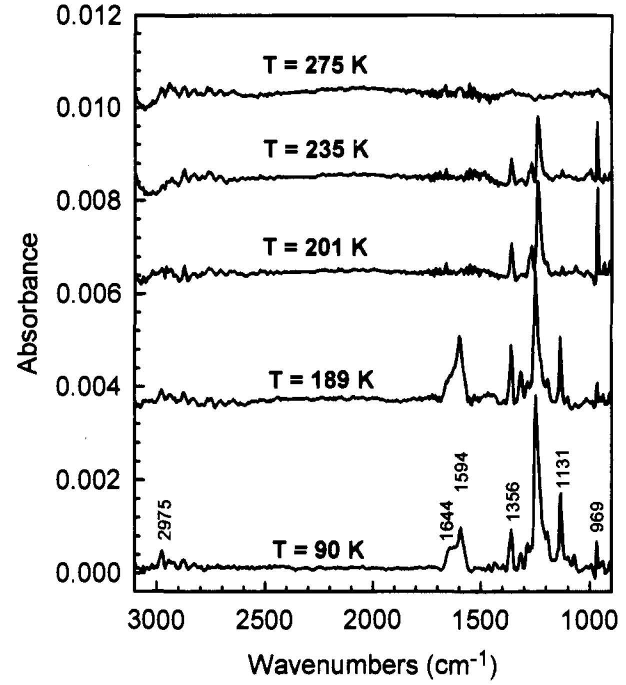

Figure 4. RAIR spectra of adsorbed fodH (1.7 L) on Ag(111) as a function of annealing temperature over the range 90–275 K.

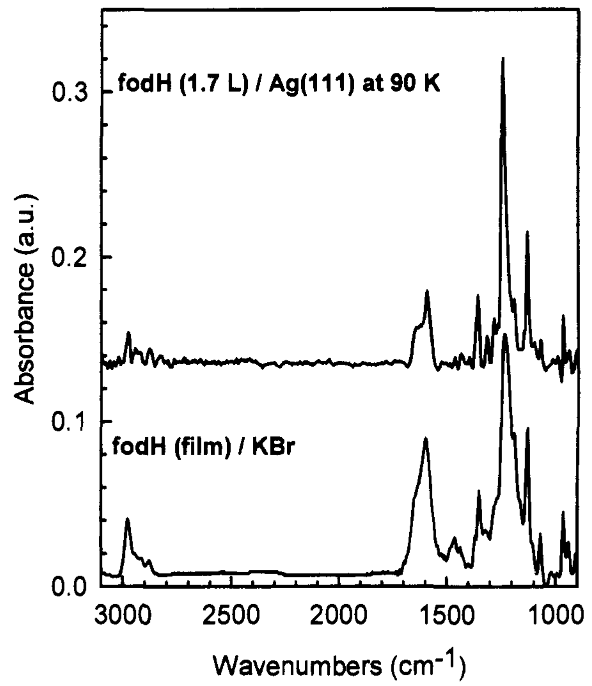

Figure 5. IR spectra of adsorbed fodH (1.7 L) on Ag(111) at 90 K compared to fodH film deposited on a KBr pellet. The latter spectrum was obtained by transmission and the resolution was 4 cm^{-1}.

chemisorbed fodH molecules (at low coverage) are oriented with their OCCCO skeletons parallel to the substrate surface. On the basis of the results of the adsorption of Cu(hfac)$_2$ on Pt(111), Parmeter[21] proposed the presence of such a structure in the case of the adsorption of hexafluoroacetylacetone (hfacH) on Pt(111). Direct thermal desorption on the chemisorbed layer of hfacH from Pt(111) is impossible because it dissociates. The confirmation of the adsorption of such a structure by β-diketones on metal surfaces at low coverages comes from the variation observed in the RAIR spectra as a function of Ag(111) anneal temperature. Figure 4 presents an outline of these changes. We note the complete disappearance of ν(C=O) and ν(C=C) vibrational modes at a temperature of 201 K, which coincides with the desorption of the multilayer as established by the TPD data (Figures 1 and 2). Therefore, the RAIR spectrum obtained at 235 K (Figure 4) represents the vibrational spectrum of the adsorbed fodH molecules having their OCCCO skeletons parallel to the surface. In fact, the chemisorbed phase desorbs at 250 K. Consistent with the TPD results, RAIRS data indicate that fodH molecules do not dissociate on Ag(111); all vibrational bands disappeared after the desorption of the chemisorbed layer. The FTIR measurements confirm then that the adsorption of fodH on Ag(111) is not a dissociative process.

The adoption of the flat-laying structure by fodH molecules on Ag(111) is due to an intramolecular rearrangement. The absence of a doublet due to ν(C=O) at 1720 cm^{-1}[22] is an indication that fodH exists on the Ag(111) surface in the enol form and that the keto–enol tautomer equilibrium is displaced to the enol form. The spectra of the fodH multilayer on Ag(111) and a fodH film on a KBr disk obtained by transmission are very similar (Figure 5) and support this argument. In neither spectra is there any evidence of the existence of vibrational peaks in the range 1700–1800 cm^{-1}. The main conclusion that we can draw from this study is that the β-diketone molecules adsorb first on metal surfaces with their OCCCO plane parallel to the substrate surface as a result of the intramolecular rearrangement which led to the enol entity formation.

We noted a small upward shift (10–16 cm^{-1}) of the ν(C–F) vibrational bands of the condensed phase in comparison with the chemisorbed layer. The C–F stretches are also sensitive to the local environment. This shift could be a consequence of the lateral interactions between the C–F oscillators. However, the coupling between the C–C and C–F motions for these species may also be sufficient to account for the observed shift. Dipole couplings are known to cause an upward shift of vibrational frequencies. For example, the reported vaues for CO and NO on Pt(111) are 35 and 5–33 cm^{-1}, respectively.[20]

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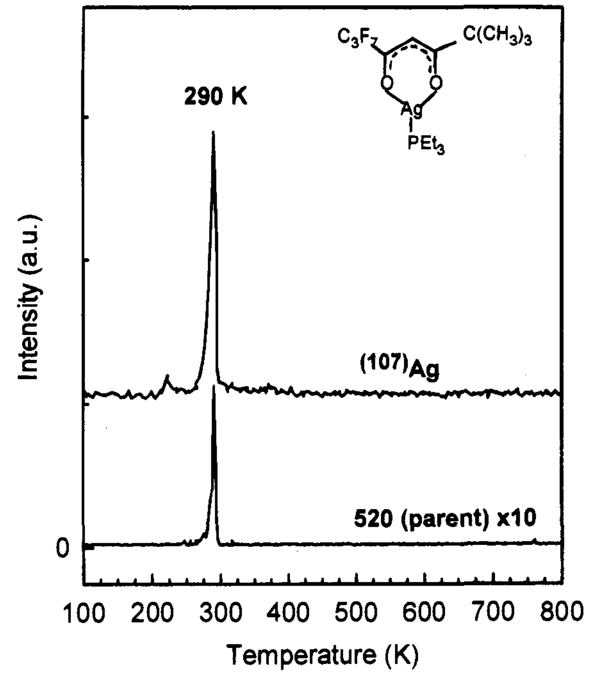

Figure 6. TPD spectra recorded after exposing Ag(111) at 90 K to 0.5 L of (fod)AgPEt$_3$. Traces for mass 520 (parent peak) and mass 107 (^{107}Ag isotope) are shown. The spectrum of the parent peak is magnified by 10.

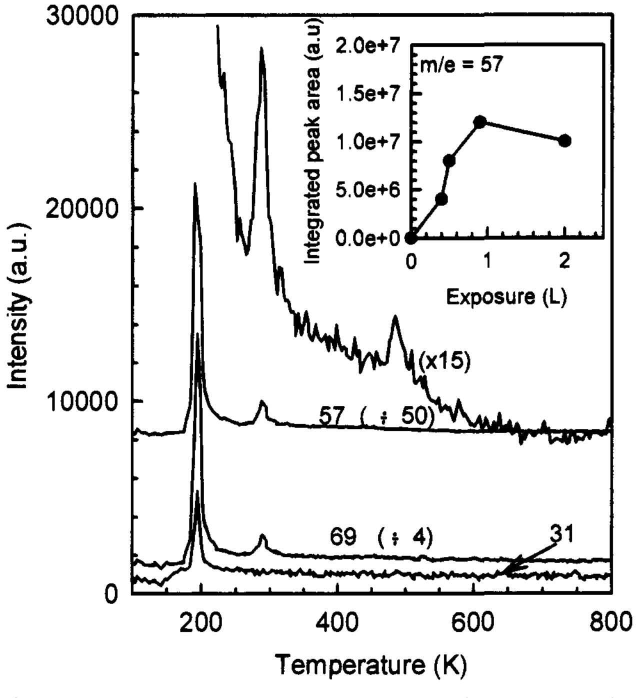

Figure 7. TPD spectra of masses 57 (C(CH$_3$)$_3$) (/50), 69 (CF$_3$) (/4), and 31 (CF) following the adsorption of 0.5 L of (fod)AgPEt$_3$ on Ag(111) at 90 K.

(B) Adsorption of (fod)AgPEt$_3$ on Ag(111). TPD Results of the Adsorption of (fod)AgPEt$_3$ on Ag(111). Thermal desorption data of (fod)AgPEt$_3$ adsorbed on Ag(111) at 90 K are shown in Figures 6 and 7. The first interesting observation is the molecular desorption of (fod)AgPEt$_3$, mass 520 amu, at 290 K (Figure 6). This result confirms that this precursor can reach the substrate surface without any decomposition in the gas phase. The thermal stability of precursors is an important parameter in CVD processes since the loss of selective deposition on patterned substrates may result from precursor decomposition in the gas phase. The selectivity depends on the nucleation processes, and therefore, precursor decomposition in the gas phase may favor the intrinsic nucleation (metal cluster formation).[23] The thermal stability of the precursors then assures that the process of metal deposition is a function of the nature of the substrate and not a function of events taking place in the gas phase. The molecular desorption peak is confirmed by the detection at the same temperature of masses 107 and 109 amu with roughly equal intensities, as expected since the two isotopes of silver have approximately the same natural abundance, 51.83% and 48.17% for ^{107}Ag and ^{109}Ag, respectively.[4] The molecular desorption peak exhibits zero-order desorption kinetics with an activation energy of desorption of 84 kJ·mol^{-1}, assuming that the pre-exponential factor is 10^{13} s^{-1} for $\beta = 2$ K·s^{-1}.

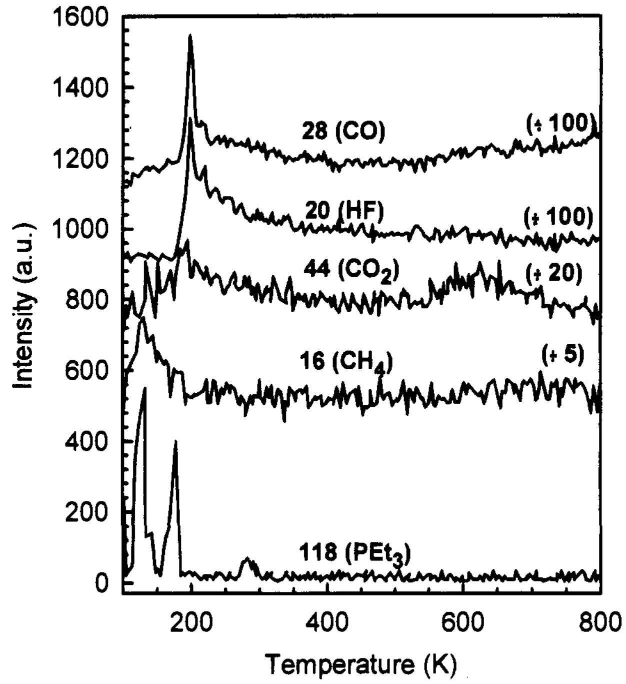

Figure 8. TPD spectra of masses 28 (CO) (/100), 20 (HF) (/100), 44 (CO$_2$), 16 (CH$_4$), and 118 (PEt$_3$) after dosing Ag(111) at 90 K with 0.5 L of (fod)AgPEt$_3$.

A number of fragments[19] have been followed during TPD cycles. Figures 7 and 8 display TPD spectra of selected masses: 57 (C(CH$_3$)$_3$ and/or C$_2$HO$_2$)), 69 (CF$_3$ and/or CO-CHCO), 31 (CF and/or P), 44 (CO$_2$), 28 (CO), 20 (HF), 16 (CH$_4$), and 118 (PEt$_3$). The detected masses 57, 69, and 118 amu at 290 K result from (fod)AgPEt$_3$ fragmentation in the ionization zone of the mass spectrometer. However, the presence of additional features in the TPD spectra of masses 57, 69, and 118 amu at 200 K which are not accompanied by the thermal desorption of the parent fragment indicates that a part of the precursor undergoes dissociation in the adsorbed phase. Further confirmation of this dissociation is provided by the desorption of masses 16 (CH$_4$) and 118 (PEt$_3$).

fodH was identified as the major desorbing species at 200 K. In some TPD runs a small desorption peak of mass 296 was observed at this temperature. The recorded relative intensities (integrated peak areas) of masses 57, 29, 69, 296, and 169 are 100, 10.8, 6.1, 1.4, and 0.14%, respectively. These values are in good agreements with those obtained during fodH admission into the UHV chamber. On clean Ag(111), fodH desorbs molecularly from the multilayer at 197 K and from the chemisorbed layer at 250 K. The formation and the desorption of fodH thus implies the presence of atomic hydrogen on the

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surface. Adsorbed atomic hydrogen may result from the readsorption of residual gas or more probably from the decomposition of other intermediates. The desorption of CH_4 at low temperature supports the hypothesis that a part of the ligands dissociated. The shape of the CH_4 desorption peak is characteristic of species generated upon pyrolysis.[24] Another possible explanation of the origin of fodH which must be considered is its adsorption during exposure of the sample to the Ag precursor, which might be contaminated by traces of fodH. If the latter explanation is correct, the higher volatility of fodH will certainly favor first the formation of the chemisorbed state which desorbs at 250 K rather than the physisorbed state (T_p = 197 K). Additional support for fodH formation following the precursor dissociation in the adsorbed phase comes from the intensity of mass 57 amu (the most abundant fragment of fodH), which seems to reach saturation with increasing exposure as shown in the inset of Figure 7. Therefore, we can consider that fodH desorption is mainly due to the thermal dissociation of the $(fod)AgPEt_3$ molecules on the surface.

It is obvious that the decomposition process of such molecules is not simple and complex intermediates coexist on the surface. The thermal desorption spectra of masses 57 ($C(CH_3)_3$), 69 (CF_3), and 29 (C_2H_5 and/or CHO) are identical and show an additional feature at 490 K with very low intensity (Figure 7). Moreover, at this temperature we observe the desorption of masses 100 (C_2F_4), 169 (C_3F_7), 170 (HC_3F_7), 20 (HF), and 58 ($HC(CH_3)_3$). The analysis of these results suggests that $C(CH_3)_3^•$ and ($C_3F_7^•$) radicals are the desorbing species upon the pyrolysis of intermediates. In fact, comparison of the relative intensities of masses 57 (100%), 58 (28%), 29 (20%), and 30 (1.0%) with published data[25,26] revealed that these fragments correspond neither to neopentane nor to isobutane and the detection of mass 58 ($HC(CH_3)_3$) is mainly due to the gas-phase reaction between atomic hydrogen and $C(CH_3)_3^•$ radicals. Similarly, the comparison of the relative intensities of masses 69 (100%), 31 (12%), 119 (5.5%), 169 (3.0%), and 170 (1.6%) does not correspond to any reported data and the detection of mass 170 is also due to the gas-phase reaction between atomic hydrogen and $C_3F_7^•$ radicals. The stability or long life time of these radicals allows them to reach the mass spectrometer. A few studies have reported the detection of radicals desorbing from metallic surfaces during TPD cycles, for example, CCl_2 from Fe(110),[27] CH_2 from H/Al(111)[28] and Pd(110),[29] CH_3O from O/Mo(110),[30] and more recently CF_3 from Ag(111)[31] and CF_2 from Pt(111).[32] However, it is the first time to our knowledge that large radicals like $C(CH_3)_3^•$ and $C_3F_7^•$ have been observed to desorb from metallic surfaces. The calculated activation energy of desorption of these species is 144 $kJ·mol^{-1}$ assuming that the desorption reaction exhibits first-order kinetics and the preexponential is 10^{13} s^{-1}. The desorption of such fragments is a direct indication that silver has been deposited and that large fragments resulting from ligand dissociation remain on the surface at high temperature. Additional evidence on Ag film formation at low temperature has been obtained from the $(fod)AgPEt_3/Pt(111)$ system since we recorded the thermal desorption of Ag atoms. The results of the surface reaction of $(fod)AgPEt_3$ on Pt(111) are given elsewhere.[33]

Table 1. Observed Vibrational Frequencies and Band Assignments for $(fod)AgPEt_3$[a]

band assignment	$(fod)AgPEt_3$ in KBr	$(fod)AgPEt_3$ on Ag(111) at 90 K
$\nu_a(CH_3)$	2957 s	2975 w
$\nu_a(CH_2)$	2930 m	2945 w
$\nu_s(CH_3)$	2907 m	2922 w
$\nu_s(CH_2)$	2879 M	2883 w
$\nu(C{=}O)$	1631 vs	1636 vs
$\nu(C{=}C)$	1580 vw	1594 vw
$\delta(CH_3)$	1535 m, 1493 vs	1535 vw, 1487 w
$\nu(CC) + \delta(CH_2)$	nr	1462 w, 1439 vw
$\nu(CCF_3)$	1395 vw, 1345 s	1395 vw, 1354 m
$\delta(CH_3)$	1345 s, 1316 vw	1354 m, 1316 w
$\nu_a(CF_2)$	1267 m	1285 m
$\nu_a(CF_3)$	1221 vs	1243 vs
$\nu_s(CF_3)$	1177 m	1204 m, 1192 m
$\nu(C{-}C) + \delta(CH)$	1155 m, 1115 m	1162 m, 1131 m
$\varrho(CH_3)$	1046 w, 962 w	1069 w, 969 w
$\varrho(CH_2)$	941 w	934 w

[a] All frequencies are given in cm^{-1}. The assignments of these bands are based on reported data of species containing such groups:[6,21,34-40] nr, not resolved; v, very; s, strong; m, medium; w, weak.

RAIRS Results of the Adsorption of $(fod)AgPEt_3$ on Ag(111). As in the case of the fodH/Ag(111) system at low exposure, the RAIR spectra obtained at low doses of $(fod)AgPEt_3$ do not show any features near 1600 cm^{-1}. This observation suggests that the first adsorbed molecules of $(fod)AgPEt_3$ on Ag(111) are bonded to the substrate with their molecular plane parallel to the surface. The adoption of such a structure for the first layer is expected since $(fod)AgPEt_3$ is a trigonal planar molecule. Proposed assignments of the IR bands for $(fod)AgPEt_3$ in a KBr pellet and adsorbed on Ag(111) at 90 K are given in Table 1. The assignment of these bands is based on reported data obtained with high-resolution electron energy loss spectroscopy (HREELS) and RAIRS for fluorinated β-diketone complexes particularly hfacH and also on recent work on perfluorocarbon molecules as well as complexes containing species such as CH_3, CCH_3, CCH_2, CF_2, CF_3, and CF_2CF_3.[6,21,34-40] The attribution of the vibrational modes to the observed bands is not a simple task since approximately 150 vibrational modes are expected. We assigned the vibrational bands at 1636 and 1594 cm^{-1} to C=O and C=C stretching modes, respectively. In this domain of frequencies for hfacH and hfac–metal complexes, the band at higher frequency was always assigned to the C=C stretch whereas the lower frequency was attributed to the C=O stretch. The attribution of these bands has been a subject of controversy.[34,36] Our assignment of these bands is supported by the changes occurring in the RAIR spectra as a function of substrate temperature and on the natural strength of the C=O dipole moment compared to that of the C=C bond.

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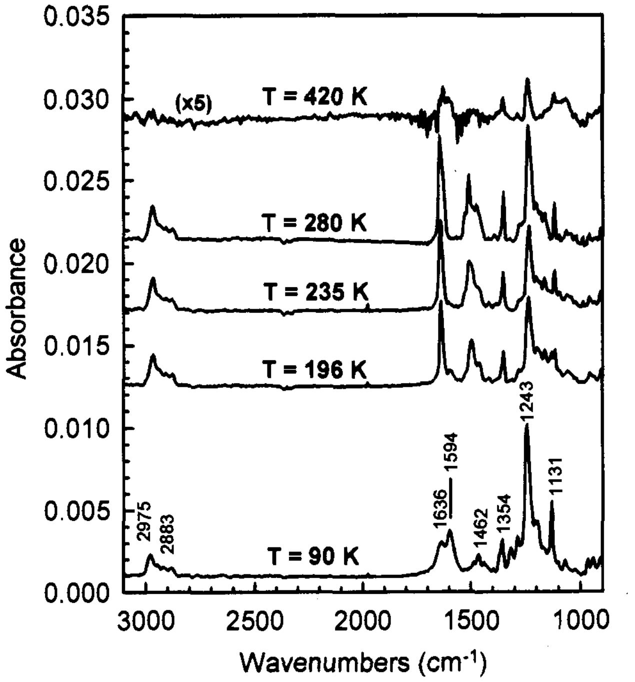

Figure 9. Evolution of RAIR spectra of adsorbed (fod)AgPEt$_3$ (0.5 L) on Ag(111) with the annealing temperature over the range 90–420 K.

A general outline of the thermal evolution of RAIR spectra following the adsorption 0.5 L of (fod)AgPEt$_3$ on Ag(111) is shown in Figure 9. We observe important changes in the IR spectra between 90 and 280 K in all regions of the spectrum, the most apparent occurring in the ν(C=O) and ν(C=C) region near 1600 cm^{-1}. In order to highlight these changes we plotted the variation of the integrated peak areas of the vibrational bands versus the annealing temperature (Figure 10). Indeed, the increase of Ag(111) crystal temperature from 90 to 190 K is accompanied by an increase of all integrated bands and their drop near 200 K as illustrated in Figure 10. The initial increase in peak intensities can be explained by reorientation of intermediates resulting from the dissociation of adsorbed (fod)-AgPEt$_3$ molecules having their molecular plane parallel to the surface. The decrease in the integrated vibrational bands around 200 K corresponds to the first desorption peak as shown in the TPD results.

Heating of the Ag(111) crystal from 200 to 280 K led to an enhancement of all the vibrational bands (Figure 9). This thermally induced change of all vibrational bands implies that they all belong to the same adsorbed species. Molecular desorption of (fod)AgPEt$_3$ as indicated by the desorption of the parent fragment (mass 520 amu) at 290 K (Figure 6) as well as a decrease in the intensities of the IR bands around this temperature, support the hypothesis that some precursor is still intact on the surface. As shown in Figure 11, RAIR spectra of (fod)AgPEt$_3$ on Ag(111) obtained between 200 and 280 K and the FTIR transmission spectrum of (fod)AgPEt$_3$ in a KBr pellet are similar. Following substrate annealing from 200 to 280 K, the ν(C=O) stretching band is shifted to 1640 cm^{-1}. More importantly, the annealing over this range of temperature (200–280 K) leads to an reorientation of the (fod)AgPEt$_3$ molecular plane. This reorientation or reorganization of the adlayer may be the consequence of unfavorable intermolecular interactions due to steric effects between coadsorbed species. The adoption of the new conformation becomes possible only after byproduct desorption at 200 K. A number of studies have reported changes in the orientation of adsorbates with respect to the surface normal as a function of the coverage or following substrate warming. Debe[41] has developed a method called RATIO for extracting information on adsorbate orientation using FTIR, and more recently Hahn[42] used a modified version of the RATIO

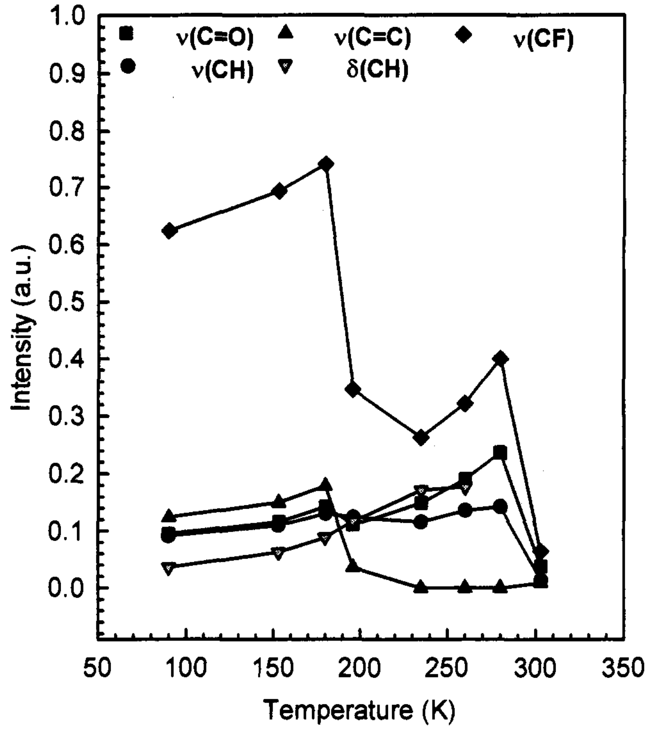

Figure 10. Variation of the integrated IR band areas of adsorbed (fod)-AgPEt$_3$ species on Ag(111) as a function of substrate temperature. ν(C–H) corresponds to the 2980–2870 cm^{-1} domain, ν(C=O) for 1640 cm^{-1} band, ν(C=C) for 1694 cm^{-1} band, δ(C–H) for 1530–1320 cm^{-1} region, and ν(C–F) for 1270–1150 cm^{-1} domain. These changes indicate that thermally induced reorganization of the adsorbed species occurs.

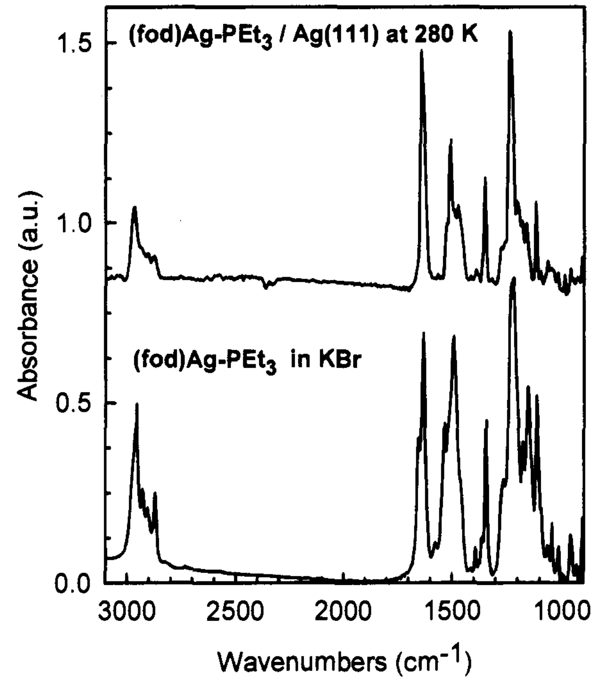

Figure 11. Comparison between a RAIR spectrum of adsorbed (fod)-AgPEt$_3$ on Ag(111) taken at 280 K with an IR spectrum of (fod)AgPEt$_3$ in KBr pellet obtained by transmission with a resolution of 4 cm^{-1}.

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method to study the orientation of pyromellitic dianhydride on Pt(111). The (fod)AgPEt$_3$ molecules which were randomly oriented at lower temperature, reorient their molecular plane to a position more nearly perpendicular to the surface in order to minimize steric effects. Opposite behavior (tilting away from the surface normal) with increasing the coverage was observed in the case of the methoxy group on Cu(100).[43] Therefore, we can consider that this new structured organometallic film on Ag(111) is an evolution toward a crystalline or ordered form. The dissociation of the remaining (fod)AgPEt$_3$ molecules (ordered layer) does not occur, the main reasons being that the fragments resulting from the dissociation of the flat-laying molecules act as site blockers because a minimum of empty neighbor sites are necessary for the decomposition reaction.

Subsequent substrate heating beyond 300 K leads to the disappearance of the vibrational peaks related to the presence of molecular (fod)AgPEt$_3$. The shape and peak positions of the remaining features are completely different from those recorded before molecular desorption. The RAIRS data however indicate that CH$_3$ and C$_3$F$_7$ moieties remain on the surface above 400 K; ν(C−H) at 2980 cm^{-1}, δ(CH$_3$) at 1351 cm^{-1}, and ν(CF$_3$) at 1236 cm^{-1} are present. Additional features consisting of one peak centered at 1628 cm^{-1} ν(C=O) and a shoulder at 1600 cm^{-1} ν(C=C) are also present. These results corroborate the TPD measurements concerning the possible desorption of C(CH$_3$)$_3^\bullet$ and C$_3$F$_7^\bullet$ radicals.

On the basis of TPD results and supported by RAIRS data, we can summarize the interaction the (fod)AgPEt$_3$ precursor with Ag(111) as follows: (fod)AgPEt$_3$ molecules which are adsorbed flat on the surface dissociate to give fodH as the main byproduct and HF, C(CH$_3$)$_3^\bullet$, C$_3$F$_7^\bullet$, and CO$_2$ as the secondary byproducts. The generation of the secondary byproducts is due to the lack of a reducing agent such as hydrogen or water, which are used to enhance the purity of the deposited metallic films. However, we have no evidence that the tilted (fod)AgPEt$_3$ molecules undergo decomposition. An attempt to describe the reaction paths of adsorbed phases is given below:

$$\mathrm{(fod)AgPEt_{3(ads)}} \xrightarrow{\mathrm{T > 100\ K}} \mathrm{Ag_{(ads)} + fod_{(ads)} + PEt_{3(ads)} + (fod)AgPEt_{3(ads)}} \tag{1}$$

$$\xrightarrow{\mathrm{130-170\ K}} \mathrm{PEt_3\ (g) + CH_4\ (g)} \tag{2}$$

$$\xrightarrow{\mathrm{200\ K}} \mathrm{fodH\ (g) + (CHO)_{x(ads)} + (CF)_{y(ads)}} \tag{3}$$

$$\xrightarrow{\mathrm{290\ K}} \mathrm{(fod)AgPEt_3\ (g)} \tag{4}$$

$$\xrightarrow{\mathrm{490\ K}} \mathrm{C_3F_7^\bullet\ (g) + C(CH_3)_3^\bullet\ (g) + HF(g)} \tag{5}$$

$$\xrightarrow{\mathrm{600\ K}} \mathrm{CO_2\ (g) + C_{(ads)}} \tag{6}$$

Conclusions

In the present work we have shown that the first adsorbed states of the fodH and (fod)AgPEt$_3$ molecules lie parallel to the Ag(111) surface at 90 K. For higher doses they both adsorb randomly at low temperature. Upon warming the substrate, the physisorbed fodH molecules desorb at 197 K, whereas the chemisorbed layer desorbs at 250 K. No decomposition of the fodH molecules has been observed on Ag(111). In contrast to the fodH/Ag(111) system, at low coverages, the lying-down (fod)AgPEt$_3$ molecules undergo dissociation leading to the desorption of a number of species. The main byproducts desorbing at low temperature were fodH, PEt$_3$, and CH$_4$. Above room temperature we observed the desorption of HF and C$_3$F$_7^\bullet$ and C$_4$H$_9^\bullet$ radicals. The randomly oriented (fod)AgPEt$_3$ molecules at 90 K reorient their molecular plane to a position nearly perpendicular to the surface normal following substrate annealing and desorb at 290 K.

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